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A THEORETICAL STUDY OF THE COMBUSTION OF MAGNESIUM / TEFLON / VITON PYROTECHNIC COMPOSITIONS

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L.V. de YONG AND K.J. SMIT

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A Theoretical Study of the Combustion of Magnesium/Teflon/Viton Pyrotechnic Compositions

L.V. de Yong and K.J. Smit

MRL Technical Report
MRL-TR-91-25

Abstract

A theoretical study has been conducted using the NASA-Lewis CEC 76 computer code to model the combustion of pyrotechnic compositions based on magnesium/Teflon/Viton. The study examines the effect of formulation changes on the distribution of reaction products, the reaction temperature and the heat of reaction. The maximum temperature and heat are produced in the stoichiometric fuel concentration whilst the reaction products change significantly with the concentration of magnesium. The Teflon and Viton oxidizers generally have only a minor effect on the system thermodynamics.

The major reaction products are magnesium fluoride, magnesium and solid carbon. The proportion of carbon as a combustion product remains relatively constant over a large range of fuel or oxidant concentrations.

The choice of the optimal MTV composition for IR decoy applications appears to be based more on burn rate and ignitability requirements than on temperature, heat output or optimization of reaction products.

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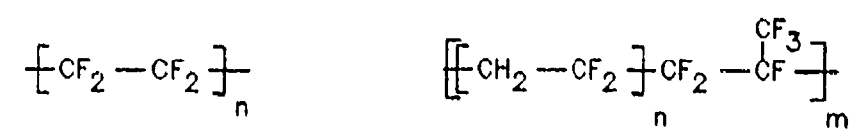
Contents

A Theoretical Study of the Combustion of Magnesium/Teflon/Viton Pyrotechnic Compositions

1. Introduction

Pyrotechnic compositions based on magnesium and Teflon (MT compositions) are extensively used for infra-red (IR) decoy flares and as igniter compositions for rocket motors. They have found wide use in these applications because of the large quantity of heat produced by the oxidation of the magnesium by fluorine in the Teflon. The heat produced by the oxidation of magnesium with gaseous fluorine is approximately - 4200 cal/gram of reactants (- 46.2 kJ/g magnesium) which is greater than the heat produced by the oxidation of magnesium with oxygen at - 3600 cal/gram of reactants (- 24.8 kJ/g magnesium). Most importantly, MT has an exceptional calorific (energy) output compared to most other fuel/oxidant mixtures due to the high heat of formation of magnesium fluoride (- 1123 kJ/mole).

For ease of processing and enhanced safety the magnesium is usually coated with another fluoropolymer, Viton (see structure), before addition to the Teflon. The Viton acts as a binder, increases the homogeneity of the mixture, increases the design latitude for fabrication of the end product, and protects the magnesium against oxidation by moisture during storage. This composition of magnesium/Teflon/Viton (MTV) has many characteristics which make it ideal for the applications mentioned above.



Teflon[1] (polytetrafluoroethylene)

Viton[1] (vinylidene fluoride/hexafluoropropylene copolymer)

[1] Trade Name, Du Pont.

MTV combustion produces gas, solid and liquid phase reaction products. These multi-phase reaction products enhance the energy transfer process, for example in a rocket motor igniter system, through the impingement of the solid and liquid products and condensation of the gaseous products onto the propellant surface. There is also a tendency for the reaction products, upon expulsion from the igniter or from the flare body, to further react with their environment (air and other gases, the solid propellant surface, ingredients and reaction products) which may enhance their effectiveness [1]. The MTV composition also produces a low brisance output due to the low percentage of the reaction products in the gaseous phase. This is advantageous for soft ignition applications such as solid propellant rocket motor ignition [2].

MTV has shown excellent environmental and thermal stability (ageing, moisture resistance, vibration, temperature etc.) and good chemical compatibility with most materials used in pyrotechnic ordnance [2, 3]. The auto-ignition temperature of MTV is also relatively high (530°C) [4] which aids in meeting safety requirements and confers a high degree of safety in its preparation and handling compared to some alternate pyrotechnic compositions. MTV can be readily fabricated in a wide variety of forms from pellets (moulded, extruded, cast, pressed) to granular powder (pressed). Finally, MTV exhibits stable burning characteristics at sub-atmospheric pressures and its burn rate shows a low temperature and pressure dependence [4].

While MTV compositions have some capability as IR decoys against some current generation anti-air missiles, more discriminating seekers will be able to reject them as potential targets. The development of improved pyrotechnic flare compositions to defeat these threats will need enhanced IR performance in either the 3 to 5 µm waveband or the 8 to 14 µm waveband. It will be necessary to first gain a sound knowledge of the performance of existing IR flare systems. This includes not only data on dynamic performance and spectral characteristics but also thermal behaviour (heat of reaction, flame temperature) and the type and distribution of the reaction products. Many studies have been conducted on MTV or MT compositions both for igniters and IR decoy systems. These have primarily focussed on the dynamic performance of the compositions (burn rate characteristics, thermoanalytical and combustion studies, and ballistic studies [1-6]) or spectral characteristics [7-10]; only limited thermochemical studies have been carried out [2-4, 6, 10].

This study presents the findings of a theoretical examination of the thermochemical behaviour of MTV pyrotechnic compositions using a computer code to model their combustion products and energetics.

2. *Thermochemical Characteristics*

As an IR radiation source, a pyrotechnic composition must generate sufficient radiation in the appropriate wavebands, generally 3 to 5 µm and/or 8 to 14 µm. The source of this radiation comes from the reaction products produced during the combustion of the pyrotechnic composition or from interaction between the reaction products and the surrounding environment. Gas reaction products

produce infrared emission from well defined vibrational transitions, the spectral frequency being dependent on the molecular vibration excited, while condensed phase products usually release energy as grey body emission, the emission spectrum being dependent only on the temperature, or as selected grey body emission which depends also on the molecular structure and physical properties of the particle or droplet. Consequently, the reaction (flame) temperature, heat of reaction, and reaction product distribution were the main features considered in this study.

Where air was included in the calculations as a reactant, its composition was assumed to be 79% N_2 and 21% O_2. All percentages of reactants and products are mass percentage of the total mass.

3. *Computer Code*

Many computer codes exist for modelling the combustion of propellants, explosives (detonation and shock) and pyrotechnics. They have been used for pyrotechnic compositions, the most well known being the BLAKE code [11], the PEP code [12] and the NASA-Lewis CEC76 code [13]. The CEC76 code was used for this study because of its significantly greater data base, its superior capability for handling condensed phase or condensible reaction products, and its proven ability with pyrotechnic compositions [14-17]. The CEC76 code uses a free energy minimization technique to determine the condition for chemical equilibrium.

As with all thermodynamic codes, the CEC76 code has several practical limitations. The assumption of equilibrium, an ideal equation of state and the consideration of only thermodynamic, as opposed to kinetic factors are the three main limitations [18, 19]. Despite these, the CEC76 code has frequently and successfully been used to predict the thermodynamic behaviour of pyrotechnic combustion for a wide range of compositions [14-17].

The heats of formation of Teflon $(C_2F_4)_n$ and Viton $(C_5H_{3.5}F_{6.5})_n$ used in this study were - 817.5 kJ/mole and - 1394.0 kJ/mole respectively [20, 21].

The majority of the computer calculations were conducted assuming adiabatic combustion.

4. *Range of MTV Compositions Examined*

In this study a comprehensive analysis of the equilibrium performance of MTV compositions was conducted for a range of formulations involving:

1. Changes in the magnesium to Teflon ratio from 0.3 to 1.8, corresponding to formulations with magnesium content from 21% to 64%;

2. Changes in the percentage of Viton from 1% to 16%;

3. Changes in the percentage of air included in the reaction from 0% to 80%.

Calculations were carried out at three external pressures; 3500 kPa, 101 kPa and 50 kPa. The pressure 3500 kPa was chosen to represent high pressure burning and it is frequently used as a standard pressure for similar calculations for pyrotechnics and propellants. The pressure 101 kPa was chosen to simulate burning at ground level (atmospheric) and 50 kPa was chosen to simulate high altitude (low pressure) burning.

Although a large range of MTV formulations were examined, we have given particular attention to the 54:30:16 formulation since this and its 61:34:5 variant are used in almost all operational IR flare and many propellant igniter systems.

5. Results

5.1 Influences on Combustion Product Distribution

5.1.1 Changes to the Fuel Fraction

Figure 1 and Table 1 show the distribution of the predicted reaction products for adiabatic combustion of MTV at 3500 kPa pressure. The percentage Viton was left constant at 16% and the magnesium and Teflon percentages were varied, covering the range 10% to 80% magnesium.

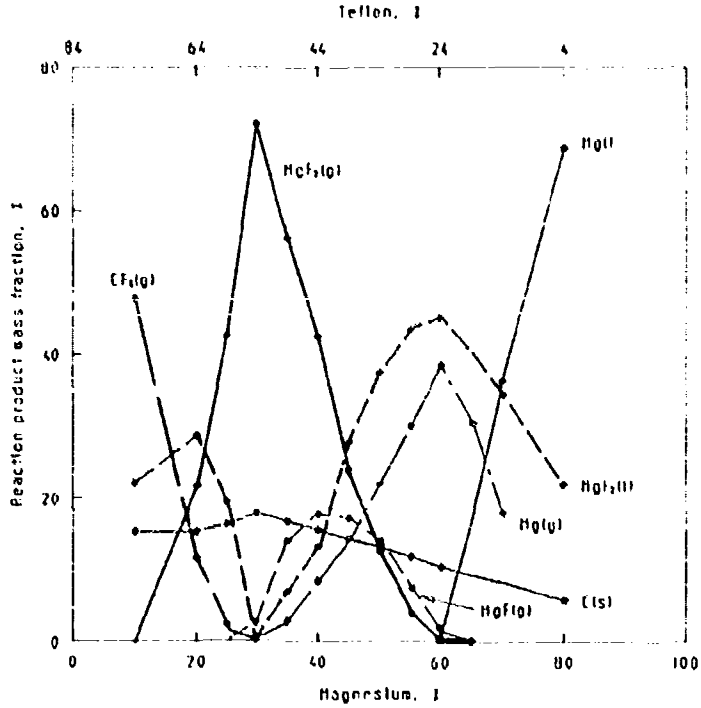


Figure 1: Change in the mass distribution of combustion products at 3500 kPa for MTV with 15% Viton and variable magnesium and Teflon mass fractions.

Table 1: Calculated Thermodynamic Properties and Reaction Products of MTV Combustion

Pressure (kPa)	% Mg	% Teflon	% Viton	Ratio of Specific Heats	Reaction Temperature (K)	Molecular Weight	Mass Fraction of Reaction Product (%)											
							C(s)	$CF_2(g)$	$CF_3(g)$	$CF_4(g)$	HF(g)	$MgF_2(l)$	$MgF_2(g)$	MgF(g)	Mg(g)	MgH(g)	MgO	$MgF_2(s)$
3500	20	64	16	1.023	3126	88.9	15.4	12.7	2.2	11.1	6.0	29.2	21.9	-	-	-	-	-
101	20	64	16	1.082	2466	65.5	16.2	7.5	0.9	17.3	6.0	0.0	51.1	-	-	-	-	-
3500	30	54	16	1.093	3547	64.2	17.9	2.0	-	-	5.8	-	72.2	2.9	0.1	-	-	-
101	30	54	16	1.088	3269	61.7	17.6	0.2	-	-	5.8	-	69.5	4.6	0.1	-	-	-
3500	40	44	16	1.092	3202	64.6	15.4	-	-	-	1.8	18.3	37.9	18.0	7.6	0.3	-	-
101	40	44	16	1.125	2572	53.5	15.7	-	-	-	2.8	-	56.7	15.4	9.2	0.1	-	-
3500	54	30	16	1.083	2651	60.3	12.3	-	-	-	0.1	42.7	5.3	8.9	28.7	1.0	-	-
101	54	30	16	1.099	2210	52.8	12.3	-	-	-	0.3	30.1	16.6	10.2	29.3	0.2	-	-
3500	60	24	16	1.097	2173	54.4	10.9	-	-	-	-	45.7	0.4	1.7	38.9	1.1	-	-
101	60	24	16	1.102	1996	51.2	10.9	-	-	-	-	41.2	3.2	3.9	40.3	0.2	-	-
3500	70	14	16	0.678	1996	108.8	8.5	-	-	-	-	34.5	0.1	0.3	17.9	0.6	37.2	-
101	70	14	16	1.131	1368	51.2	8.5	-	-	-	-	-	-	-	43.7	0.1	12.5	34.6

The major combustion products change as the percentage of magnesium in the formulation changes. If the formulation is fuel lean (< 20% magnesium), the major reaction products are C(s), CF_4(g), MgF_2(l) and MgF_2(g). There are also small amounts of CF_2(g) and HF(g) present. As the percentage of magnesium in the MTV increases, there are several changes in the equilibrium reaction products. There is a significant shift in the equilibrium between MgF_2(g) and MgF_2(l), the CF_4(g) disappears, but the mass of C(s) remains almost constant. As the formulation becomes fuel rich (> 40% magnesium) the major reaction products are MgF_2(g), MgF_2(l), MgF(s) and C(s), while Mg(g) and Mg(l) are formed from unreacted magnesium. These changes result due to shifts in the chemical equilibrium. There is also a decrease in the mass fraction of MgF(g), while the mass fraction of C(s) decreases from approximately 15% to 6% because of the loss of carbon due to the decrease in Teflon content (Viton content is constant). The presence of Mg(g) and Mg(l) confirms that the formulation is fuel rich.

When the reaction pressure is reduced to 101 kPa there is no significant change in the reaction products, although the magnesium percentage at which they first appear and their concentration change slightly (Fig. 2, Table 1). This suggests that the reaction mechanism is unchanged. The major change is the condensation of MgF_2(l) to MgF_2(s) which commences at approximately 60% magnesium.

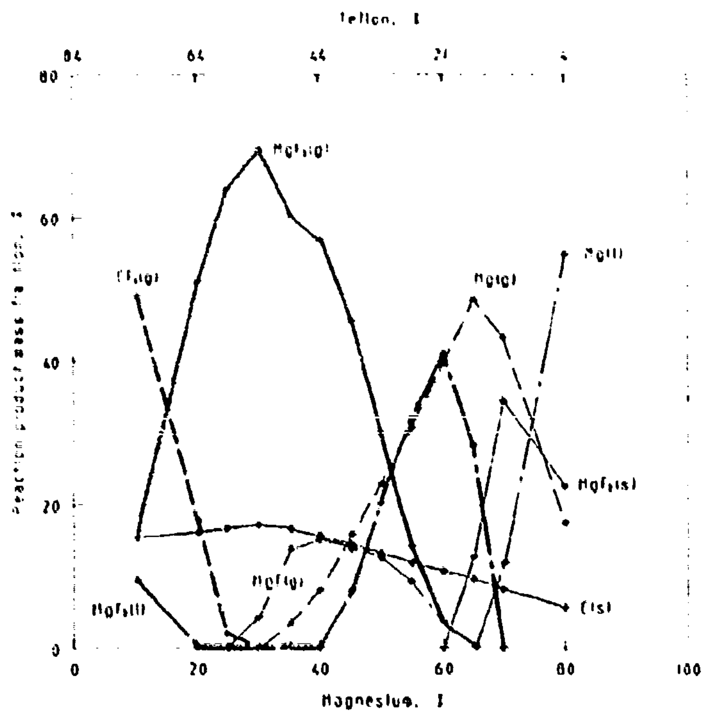


Figure 2: Change in the mass distribution of combustion products at 101 kPa for MTV with 16% Viton and variable magnesium and Teflon mass fractions.

Further reduction in reaction pressure to 50 kPa (to simulate sub-atmospheric burning), results in nearly identical reaction products to those formed at 101 kPa (Fig. 3).

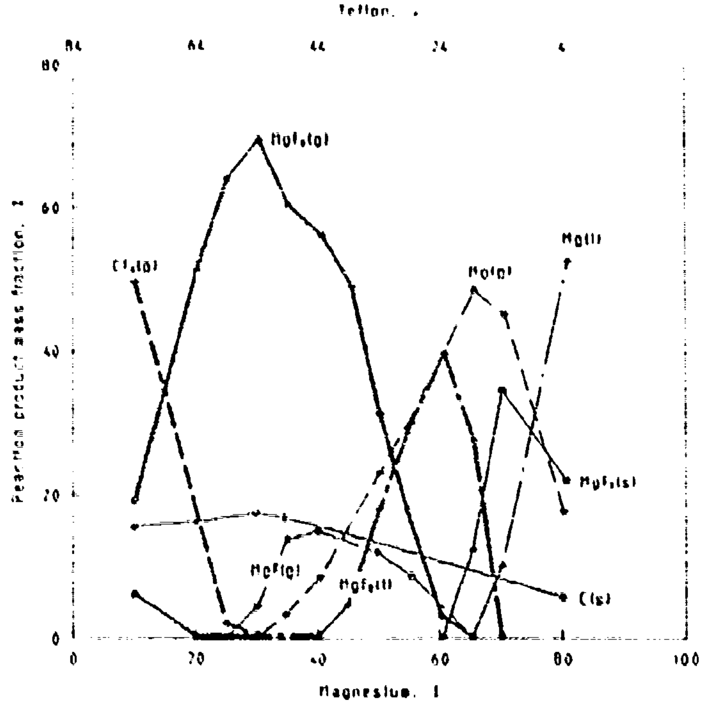


Figure 3: Change in the mass distribution of combustion products at 50 kPa for MTV with 16% Viton and variable magnesium and Teflon mass fractions.

The mass of condensed phase reaction products at all three pressures is shown in Figure 4. The initial decrease in the mass of the condensed phase reaction products is due almost exclusively to the decrease in the mass fraction of MgF_2(l) with increasing magnesium percentage (MgF_2(l) → MgF_2(g)). This is most noticeable for the reaction at 3500 kPa. Further increase in the magnesium percentage increases the mass of condensed phase products with the formation of MgF_2(l), MgF_2(s) and Mg(l). For compositions containing more than approximately 60% magnesium, more than half the reaction products are in the condensed phase.

5.1.2 *Changes to the Viton Concentration*

If the magnesium to Teflon ratio is constant and the Viton percentage varied from 1% to 10%, there is little effect on the reaction products (Figs 5, 6 and 7). This suggests that the reaction mechanism remains essentially unchanged over this range of Viton percentages.

It may however be observed that at high magnesium to Teflon ratios increases in the Viton content result in decreases in the mass fraction of MgF_2(l) and Mg(g). Similarly the proportions of MgF_2(g) and the carbonaceous products display small variations in response to changes in the Viton content.

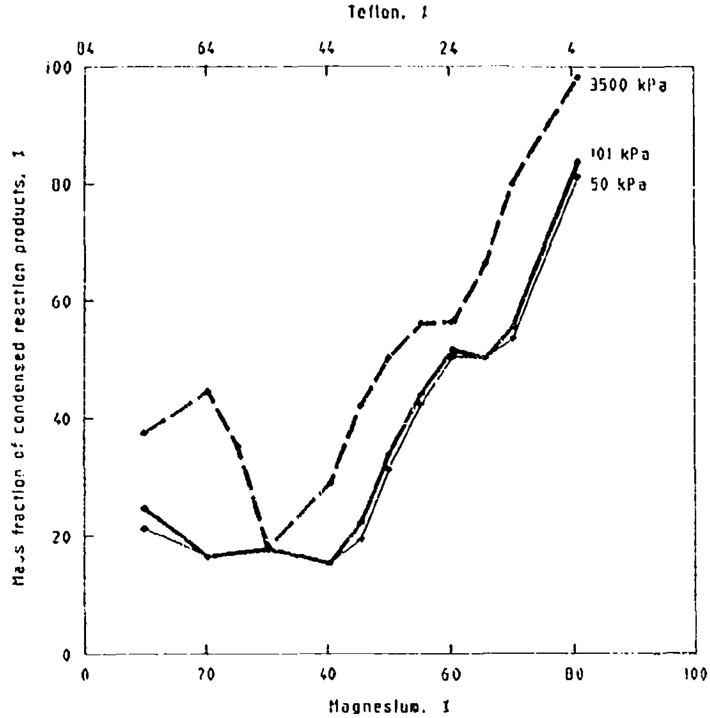


Figure 4: Change in the mass of condensed phase combustion products for MTV with 16% Viton and variable magnesium and Teflon mass fractions at 3500 kPa, 101 kPa and 50 kPa.

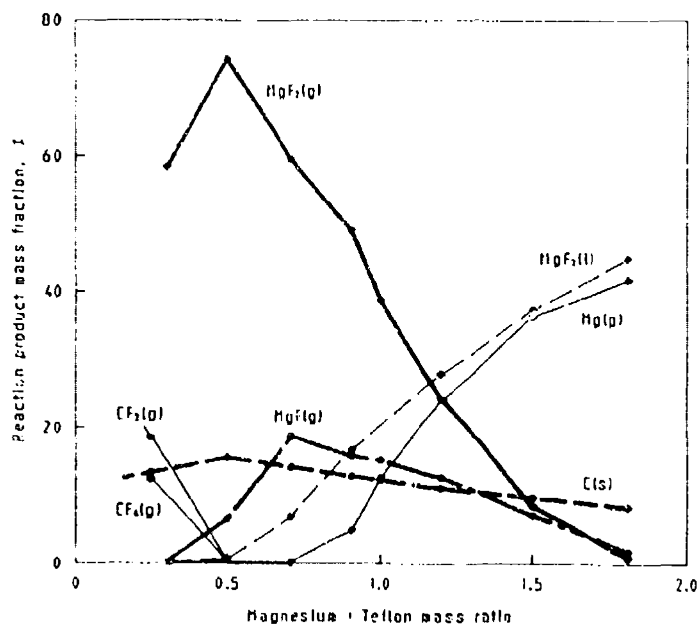


Figure 5: Mass distribution of combustion products at 101 kPa for MTV with 1% Viton and a variable magnesium:Teflon mass ratio.

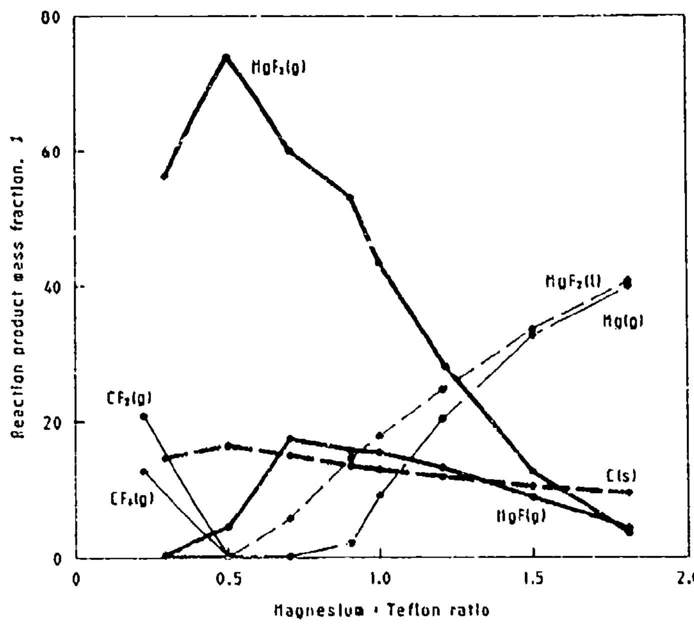


Figure 6: Mass distribution of combustion products at 101 kPa for MTV with 5% Viton and a variable magnesium:Teflon mass ratio.

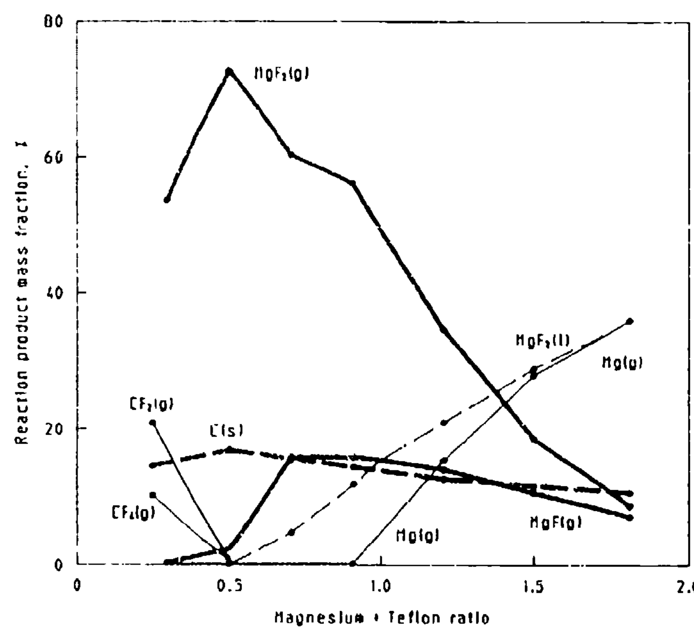


Figure 7: Mass distribution of combustion products at 101 kPa for MTV with 10% Viton and a variable magnesium:Teflon mass ratio.

5.1.3 Combustion with Air as a Reactant

MTV flares are usually burnt in air and modelling their combustion should include air as one of the reactants. Several calculations were carried out for MTV (54:30:16) at several pressures with air added as a reactant with the MTV (0% to 80% air with 100% to 20% MTV). Figures 8 and 9 show the distribution of the principle reaction products at 3500 kPa pressure.

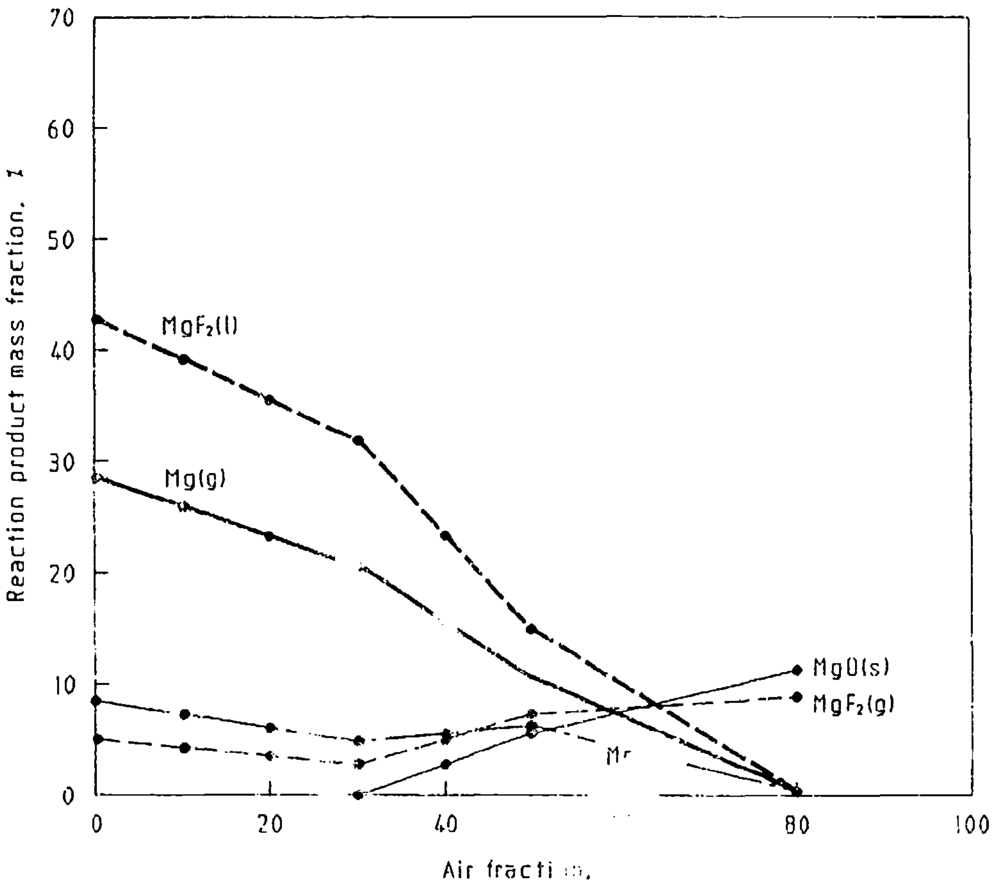


Figure 8: Variation of the mass distribution of the maximum combustion products at 3500 kPa for standard MTV (54:30:16) ... the mass fraction of air.

Figure 8 shows the preference for magnesium to react with the fluorine in the Teflon or the Viton forming predominantly $MgF_2(l)$ rather than reacting with the O_2 from the air to form MgO(s). There is excess Mg(g) for air fractions up to 80% air and although at 30% air MgO(s) begins to form, it does not constitute a significant reaction product until the amount of air is greater than 60%. As the percentage of air increases, the C(s) reaction product begins to undergo a secondary reaction with the O_2 to form CO(g) and $CO_2(g)$. The preferred reaction product at low air fractions is CO(g) but this forms $CO_2(g)$ as the amount of air increases and more O_2 becomes "available".

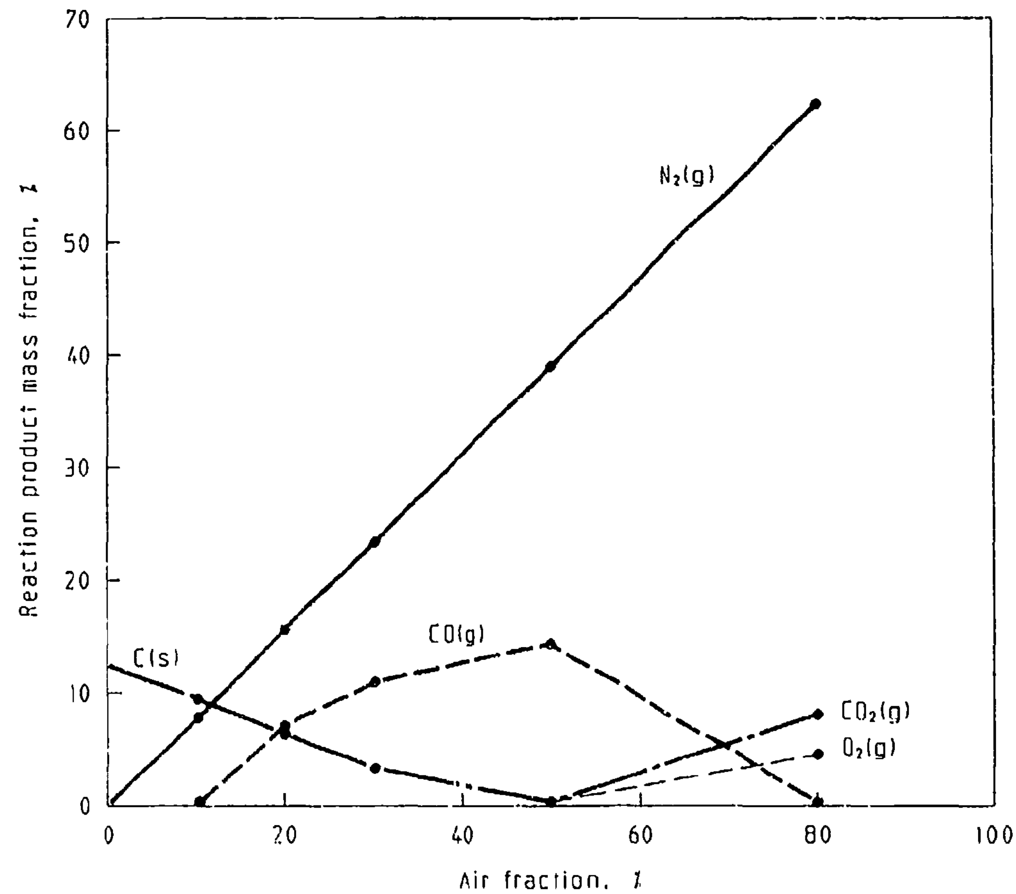


Figure 9: Variation of the mass distribution of non-magnesium combustion products at 3500 kPa for standard MTV (54:30:16) with changes in the mass fraction of air.

Reducing the pressure to 101 kPa decreases the mass fraction of MgF_2(l) and increases the mass fraction of MgF_2(g). All other reaction products remain at similar percentages to the 3500 kPa results for all air fractions.

The N_2 in the air does not appear to take part in any reactions; this is due to the limitations of the code and the lack of relevant product data in the data base (see Section 6.1).

5.1.4 Replacement of Teflon by Viton

If the magnesium content is fixed at 54% and the ratio of Teflon and Viton is varied, the major reaction products are C(s), Mg(g), MgF_2(l) and MgF_2(g). As the Teflon is replaced by Viton, the amount of C(s) increases due to the increased percentage of carbon in the Viton. The mass fraction of MgF_2(l) increases at the expense of MgF_2(g) due to an equilibrium shift. There is also a

minor increase in the amount of Mg(g) and a decrease in the amount of the MgF(g) radical. This behaviour is true at both 3500 kPa and 101 kPa reaction pressure.

5.1.5 Temperature Change

If the combustion pressure is fixed, significant changes in the composition of the reaction products occur as the temperature decreases. Figure 10 depicts this for MTV (54:30:16) at a pressure of 3500 kPa. As the temperature decreases the excess magnesium changes from the gas phase to a liquid to a solid; this is due to simple shifts in the equilibria with temperature. Similarly, the MgF_2(l) solidifies and MgF_2(s) forms below approximately 1600 K. The mass fraction of C(s) remains relatively constant at all temperatures.

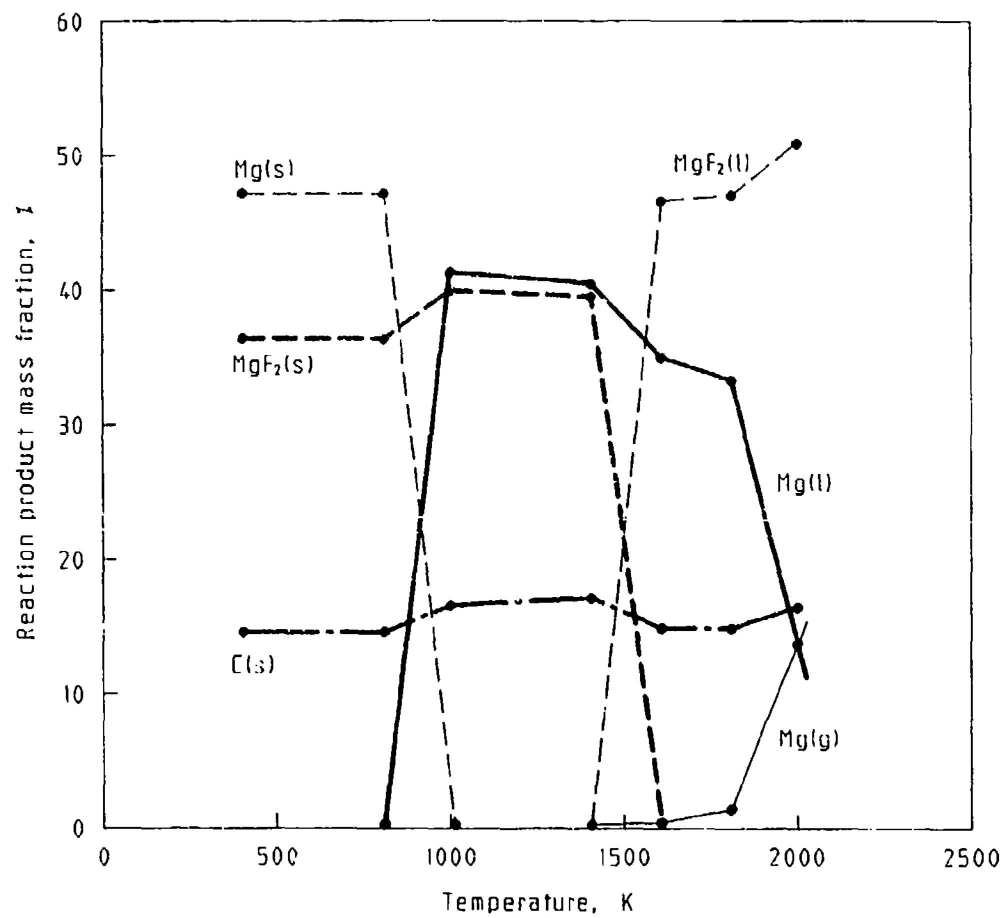


Figure 10: Change in the mass distribution of combustion products at 3500 kPa for standard MTV (54:30:16) after cooling from 2000 K to 500 K.

If the pressure is reduced to 101 kPa (Fig. 11), the excess magnesium undergoes an equilibrium shift from Mg(g) to Mg(l) to Mg(s) similar to that observed at 3500 kPa. As the temperature decreases, the mass fraction of MgF(g) and MgF_2(g) decrease and that for MgF_2(l) increases. Around 1500 K there is an equilibrium shift as MgF_2(l) solidifies to form MgF_2(s). The mass of C(s) remains relatively constant throughout the temperature range studied.

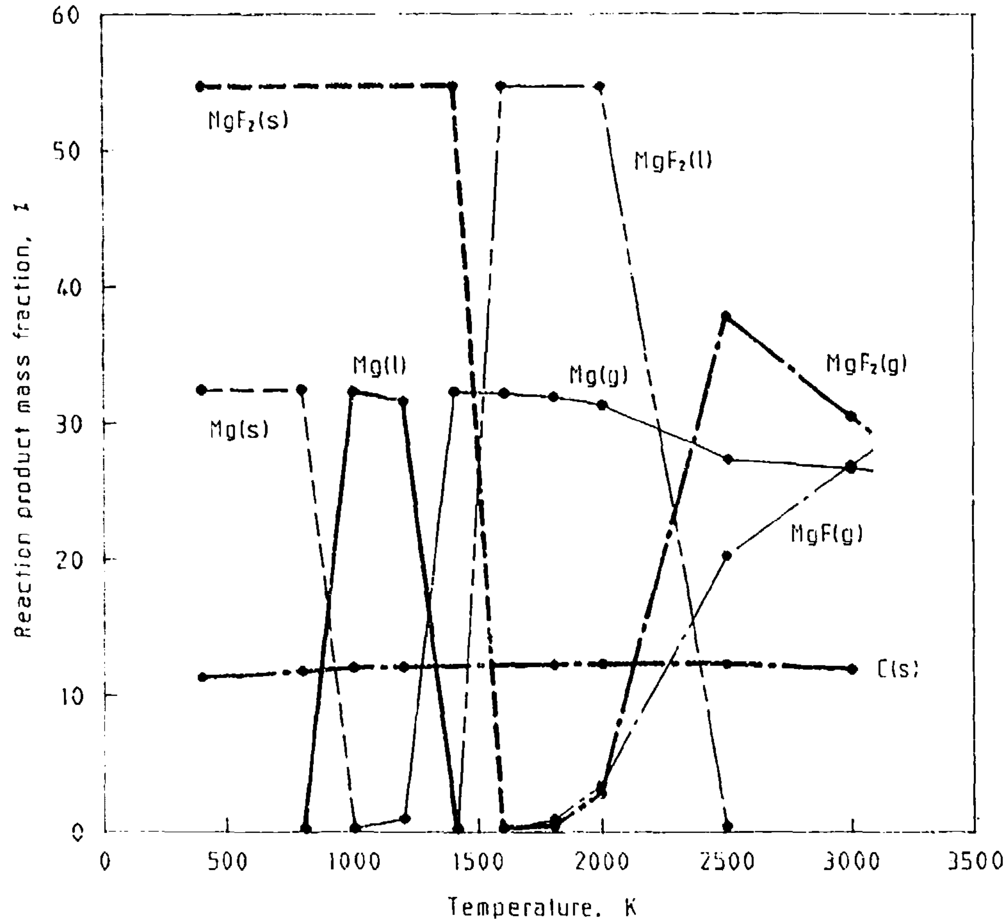


Figure 11: Change in the mass distribution of combustion products at 101 kPa for standard MTV (54:30:16) after cooling from 3000 K to 500 K.

The main differences between the reaction products at 3500 kPa and at 101 kPa are a decrease in the yield of Mg(s) formed, and an increase in the yield of MgF_2(s) produced as the temperature of the reaction products decreases.

These results indicate that the reaction products formed after expansion from the flame front to ambient temperature and pressure are MgF_2(s), Mg(s) and C(s).

5.2 *Influences on Reaction (Flame) Temperature*

5.2.1 *Changes to the Percentage Fuel*

Figure 12 displays the change in the reaction temperature with increasing magnesium and decreasing Teflon percentage (Viton constant at 16%) for MTV. The magnesium percentage for a stoichiometrically balanced system is approximately 33% which corresponds closely with the position of the maximum reaction temperature (approximately 3500 K). As the magnesium percentage increases to the stoichiometric value the reaction temperature increases and then decreases with further increases in the magnesium percentage. As the reaction pressure decreases, the reaction temperature decreases. The overall change in temperature with magnesium percentage remains similar at all pressures.

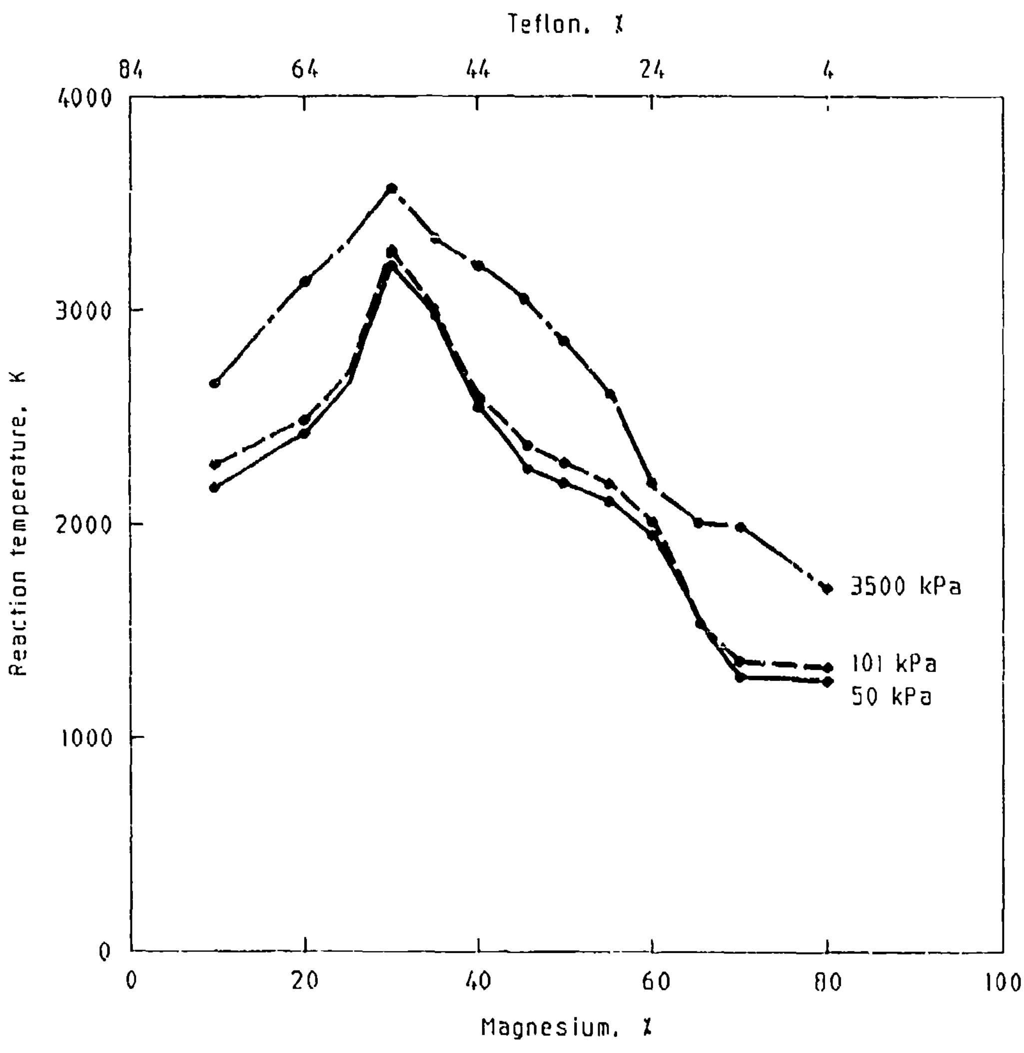


***Figure 12:** Variation of the reaction temperature for MTV (16% Viton) with change in the mass of magnesium and Teflon at 3500 kPa, 101 kPa and 50 kPa.*

Change in the reaction temperature for several magnesium to Teflon ratios at 101 kPa pressure is shown in Figure 13. The maximum reaction temperature occurs at a ratio of 0.5 (approximately 33% magnesium) for all percentages of Viton. Increasing the magnesium: Teflon ratio from 0.25 to 0.5 increases the reaction temperature. Further increase in the magnesium to Teflon ratio from 0.5 to 1.0 decreases the reaction temperature. For ratios greater than 1.0, the reaction temperature decreases at a slower rate.

The effect of Viton percentage on the reaction temperature is also depicted in Figure 13. Interestingly, large variations in the Viton content (1% to 10%) do not significantly alter the reaction temperature. The 10% Viton formulation shows a lower reaction temperature than the 5% or 1% formulations in the ratio range 0.25 to 0.5 (fuel lean). At ratios greater than 0.5 the situation is reversed. This is possibly due to the formation of $MgF_2(g)$; for ratios up to 0.5 the 10% Viton formulations show a smaller percentage $MgF_2(g)$ reaction product than for 1% and 5% formulations. At ratios greater than 0.5 the 10% Viton formulation produces more $MgF_2(g)$ than that for the 1% and 5% formulations.

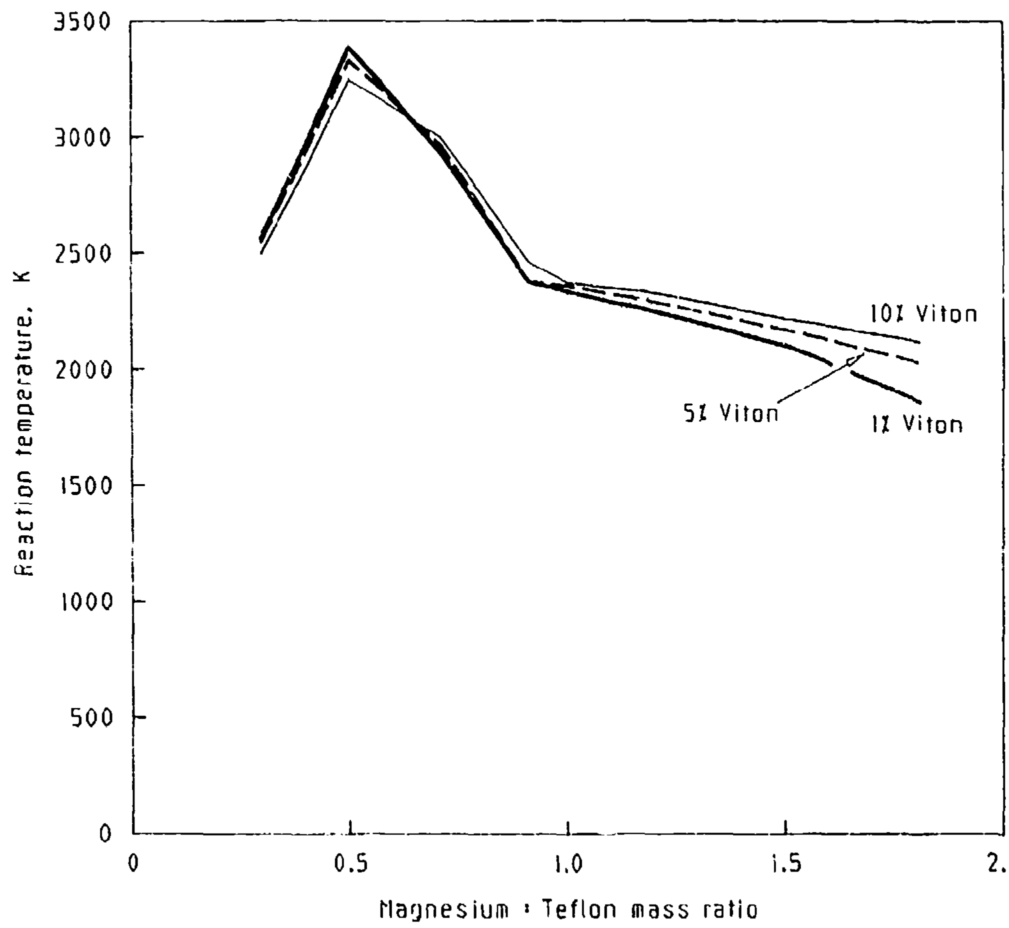


Figure 13: Variation of the reaction temperature of MTV at 101 kPa with change in the magnesium:Teflon mass ratio and Viton percentage.

As the reaction pressure decreases, the reaction temperature decreases as observed in Figure 12.

5.2.2 Air Fraction

Figure 14 shows the reaction temperature for MTV (54:30:16) with air included as a reactant. At 3500 kPa pressure, the initial reaction temperature decreases as the air fraction increases up to approximately 30% air. As more air is added, the reaction temperature increases. A similar effect occurs at lower pressures, although at low proportions of added air there is an initial increase in temperature. At all pressures the minimum reaction temperature occurs at approximately 30% air fraction, i.e. 70% MTV. Comparison of Figure 14 with Figure 12 indicates that the reaction temperature of MTV (54:30:16) can be greater in air than in the absence of air.

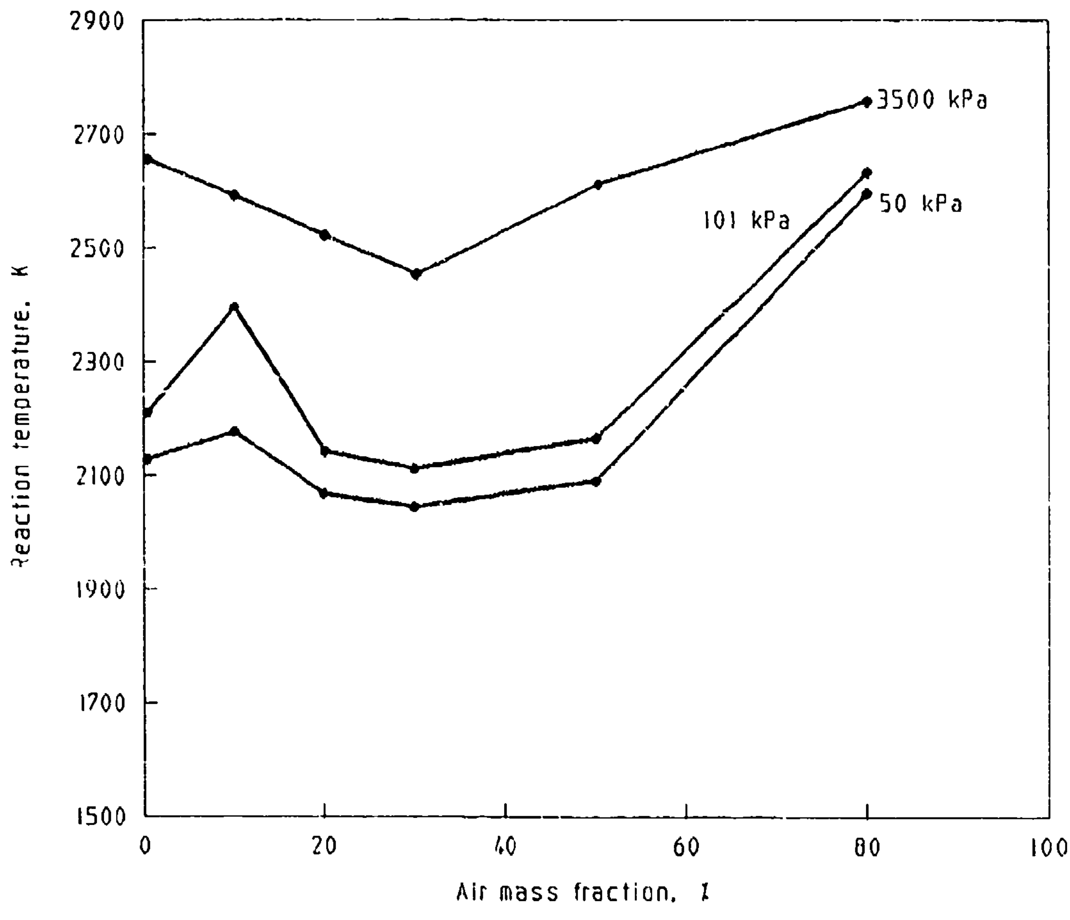


Figure 14: Variation of the reaction temperature for standard MTV (54:30:16) with change in the air mass fraction at 3500 kPa, 101 kPa and 50 kPa.

5.2.3 Changes to the Percentage of Teflon and/or Viton

If the magnesium content is fixed at 54% and the proportion of Teflon and Viton varied, then there are slight changes in the reaction temperature. At reaction pressures of 3500 kPa and 101 kPa, replacing the Viton with Teflon causes a small increase in the reaction temperature (Fig. 15). The effect is more pronounced at the higher pressure.

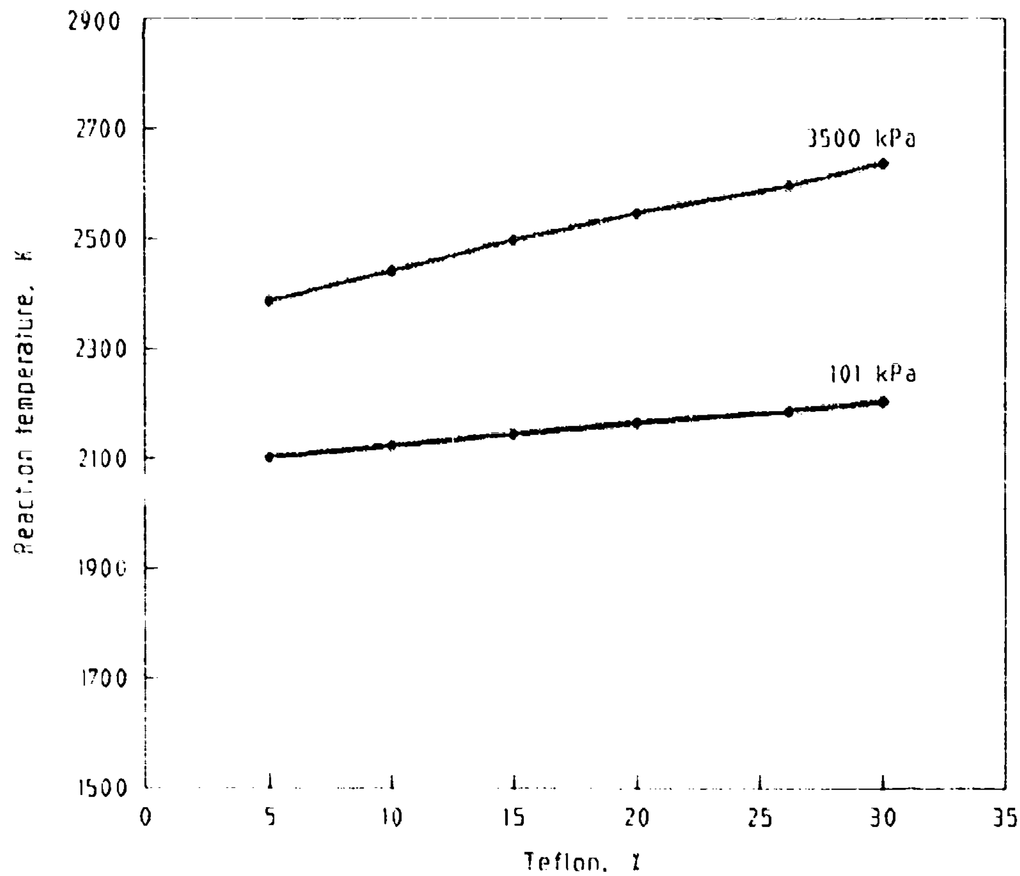


Figure 15: Change in the reaction temperature at 3500 kPa and 101 kPa of MTV containing 54% magnesium as the percentage of Teflon is increased and the percentage of Viton is decreased.

5.3 Influences on Heat of Reaction

5.3.1 Changes in the Fuel Content

The heat of reaction was calculated from the computer output from the difference in enthalpy of the reactants at 300 K and the products at the reaction temperature. This procedure has been shown to give a good estimate of the heat of reaction of pyrotechnic compositions [2, 3, 18].

Figure 16 shows that at 3500 kPa pressure the heat of reaction increases (becomes more negative) with magnesium percent to a maximum of approximately 9.2 kJ/g at about 33% magnesium level. This closely corresponds to the stoichiometric point for the reaction. Increase in magnesium beyond 33% decreases the heat of reaction. This type of behaviour is typical of many pyrotechnic compositions.

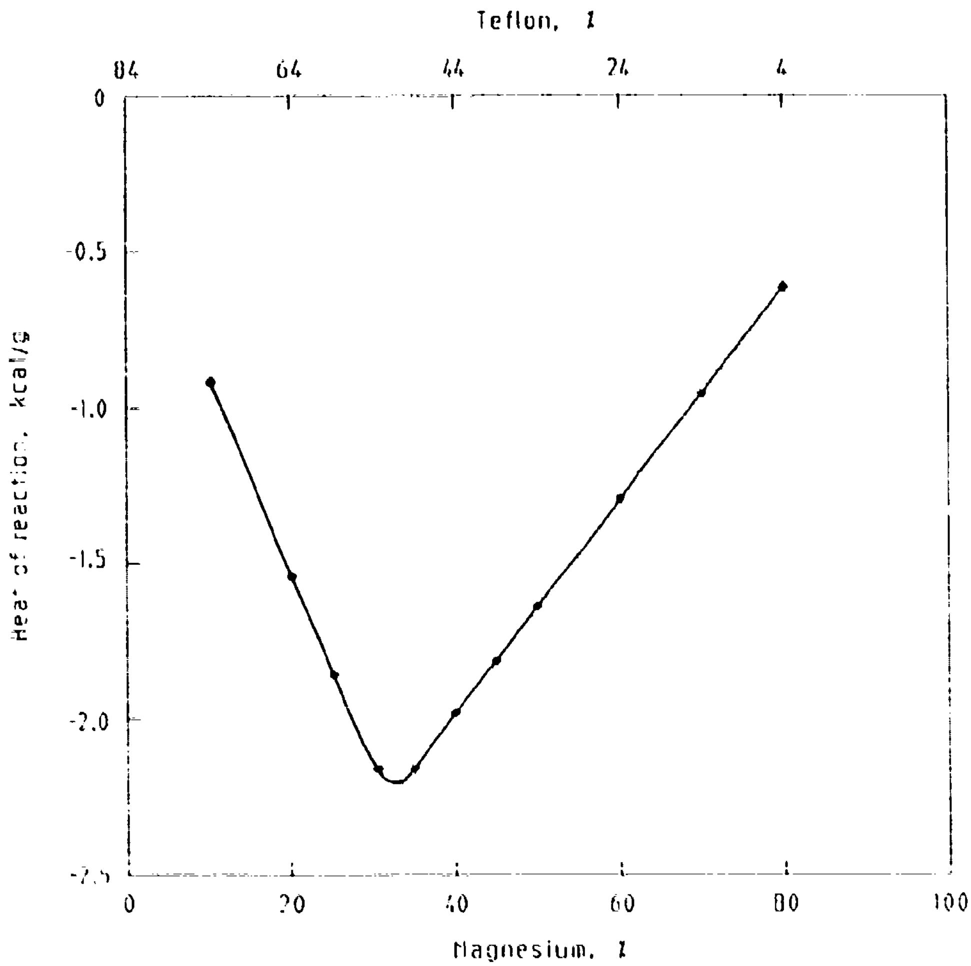


Figure 16: Heat of reaction at 3500 kPa of MTV (16% Viton) with change in the mass fraction of magnesium and Teflon.

If the proportion of Viton is altered, the heat of reaction changes marginally (Fig. 17). Interestingly, for magnesium to Teflon ratios greater than 0.9 (approximately 40% magnesium), 10% Viton formulations produce a greater heat of reaction than those with 1% Viton. For magnesium to Teflon ratios less than 0.9, the process is more complex; at some ratios the greater heat of reaction occurs for the lower Viton content formulation whilst the reverse is true at other ratios.

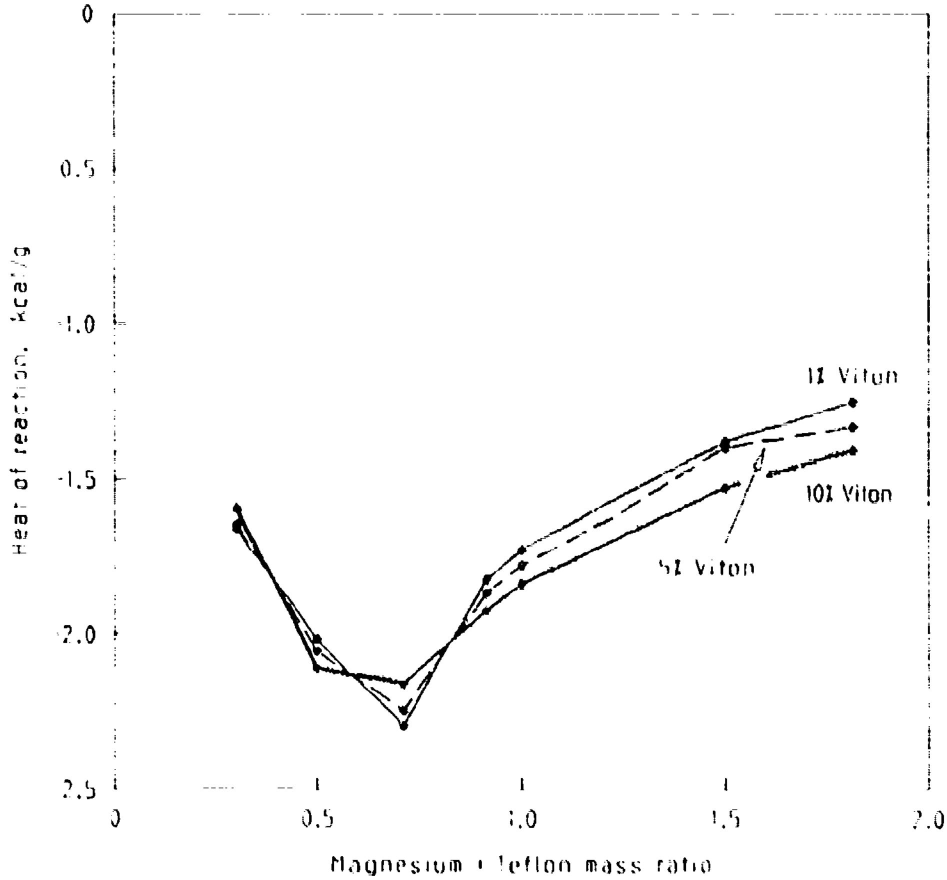


Figure 17: Variations of the heat of reaction at 3500 kPa for MTV with change in the magnesium:Teflon mass ratio and the Viton percentage.

5.3.2 *Air Fraction*

If air is added as a reactant to the MTV (54:30:16) formulation, the heat of reaction initially increases up to approximately 20% air and then decreases as further air is added (Fig. 18).

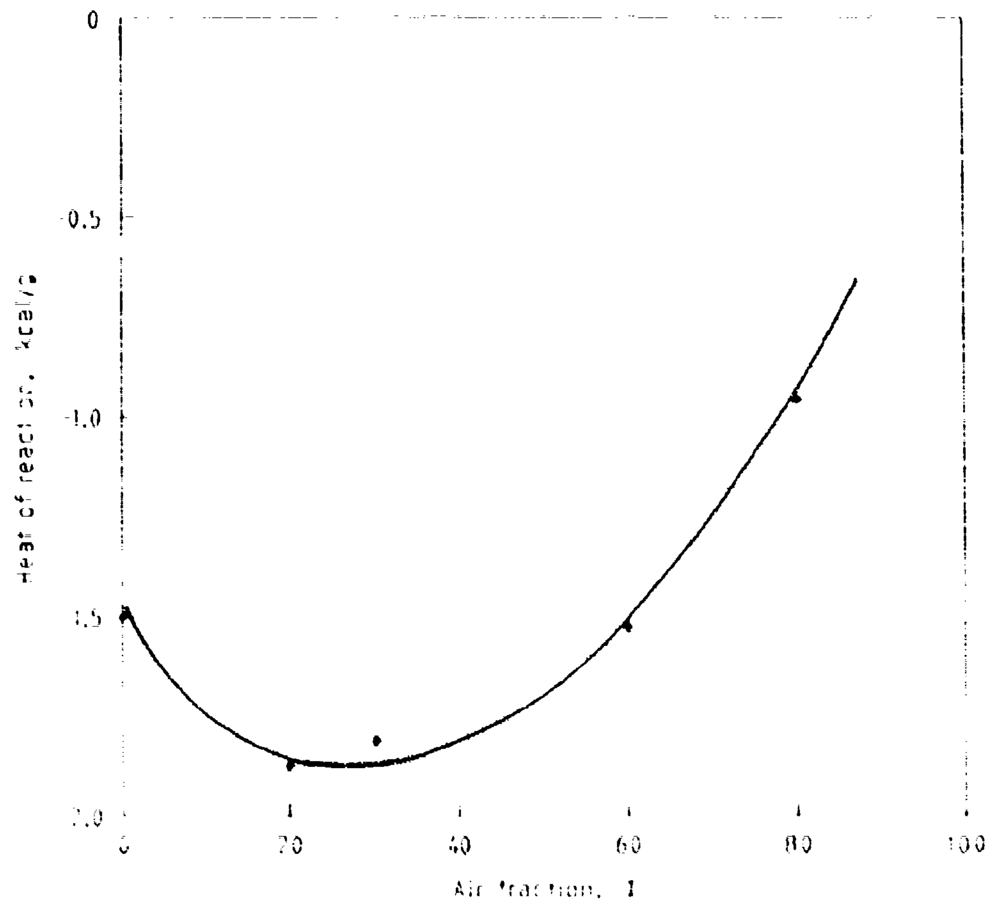


Figure 18: Variation of the heat of reaction at 3500 kPa for standard MTV (54:30:16) with change in the mass fraction of air.

6. Discussion

6.1 Reaction Products

The MTV combustion may be characterized by the following equations:

$$\text{Fuel Rich: MTV} \rightarrow MgF_2(s+g+l) + Mg(g+l) + C(s) + MgF(g) \quad (1)$$

$$\text{Fuel Lean: MTV} \rightarrow MgF_2(g+l) + C(s) + CF_4(g) \quad (2)$$

$$\text{Stoichiometric: MTV} \rightarrow MgF_2(g+l) + C(s) \quad (3)$$

As the pressure decreases, shifts in equilibrium occur causing the formation of new reaction products and different ratios of solid, liquid and gas phases of the same products. The most significant change in phase occurs with MgF_2.

These equations list only the major reaction products (each with at least 10% of the reaction product mass). The other products that form are mainly $CF_2(g)$ and HF(g). The HF(g) forms from the decomposition of the Viton which contains hydrogen. It does not form from the Teflon.

These results agree with other published studies. Peretz [4] described a simplified combustion scheme for stoichiometric and fuel rich MTV compositions by the reaction:

$$m\,Mg + C_2F_4 + nC_5H_{3.5}F_{6.5} \rightarrow (1.5n+2)MgF_2 + 3.5n\,HF + (5n+2)C + (m-1.5n-2)Mg \quad (4)$$

This equation was determined theoretically. The only additional product to our calculations (Equations (1), (2) or (3)), is HF. Our calculations (Table 1) showed that although HF(g) is present as a reaction product, in most formulations it was << 5% by mass of the total combustion products and was neglected in determining the major reactions. Thermochemical calculations based on JANAF tables have also indicated that $MgF_2(g)$ and C(s) are the principal products of combustion at the stoichiometric composition [22]. For fuel rich and fuel lean systems similar results to ours were obtained but the CEC76 code generally predicts that lower mass fractions of C(s) are formed. Kubota [5] theoretically calculated the major reaction products, at 2050 kPa, as Mg(g,l), C(s) and MgF_2(g,l). Griffiths et al. [23] studied the isothermal thermal decomposition of MT formulations using simultaneous DTA/DTG. In an inert gas (argon) the products of reaction were determined to be C(s), unreacted Mg(s), and MgF_2. These results agree with our computer predictions although Griffiths et al. also suggest that a carbon-magnesium reaction could be occurring at high temperatures (960°C). The computer code considers MgC_2 and Mg_2C_3 as possible reaction products, but it predicts that only MgC_2 forms and in such a minor amount as to be negligible ($< 5 \times 10^{-5}$ mole).

Eckstrom *et al.* [7] also conducted theoretical and experimental studies of MT combustion. He postulated that the stoichiometry of the reaction was:

$$2\,Mg + C_2F_4 \rightarrow 2\,MgF_2 + 2C(s) \tag{5}$$

For fuel rich formulations, Mg and MgF also form, although the MgF was present in only small amounts. For a fuel lean formulation CF_4 was the only additional product. These results agree very well with our results. Eckstrom's calculations also confirm our finding that the proportion of C(s) in the reaction products is almost independent of the initial MTV formulation. This is a critical result as the solid carbon is considered to be the major source of IR radiation from MTV flares. This is probably due to grey body radiation from the hot carbon particles. What is surprising is that C(s) is present in relatively small quantities (< 20%) for almost all formulations and conditions, yet this would appear to be sufficient to be successful as a decoy system. Other results from the CEC76 code indicate that for a constant fuel to oxidant ratio, replacing the Teflon with Viton, up to 10% Viton, has little effect on the reaction products except for the formation of HF(g) from the Viton.

As the temperature of the reaction products decreases from the reaction temperature to ambient, changes in the reaction products are driven predominantly by simple shifts in the chemical equilibrium. For all pressures, the major reaction products formed from the combustion of MTV and subsequent cooling to ambient temperature and pressure are MgF_2(s), Mg(s) and C(s). Combustion of MTV in air produces predominantly MgF_2 and Mg; a significant amount of MgO begins to form only when the amount of air exceeds approximately 60% of the total reactants. The proportion of C(s) decreases rapidly as the air fraction increases and disappears completely at approximately 50% air (50% MTV). This is due to the reaction:

$$3\,C + 2\,O_2 \rightarrow 2\,CO + CO_2 \tag{6}$$

This loss of carbon will have a significant effect on the performance of an IR decoy flare based on MTV.

As noted in Section 5.1.3 the N_2 in the air appears to be unreactive. This result is unexpected given that from bomb calorimetry, the heat of explosion (HOE) for MTV in N_2 is greater than in argon (1.7 kcal/gram and 1.4 kcal/gram respectively) [22]. The enhanced HOE in nitrogen has been attributed to the formation of Mg_3N_2; therefore nitrogen is not inert but takes an active part in the MTV combustion.

Examination of the computer output shows that nitrides of magnesium are not present in its data base and are therefore not considered as possible reaction products. This highlights one of the severe limitations of the use of this computer code to predict combustion processes and introduces a possible significant error in the predicted output.

Griffiths *et al.* [23] studied the decomposition of magnesium/Teflon in air and identified the reaction products as Mg, MgO and MgF_2, but no details of relative proportions of each were presented. Eckstrom *et al.* [7] also determined reaction products for MTV burnt with air in a closed bomb and reported that MgO was the predominant reaction product up to approximately

60% magnesium; then MgF_2 becomes predominant. This situation may be attributed to the influence of kinetics in the reaction; although thermodynamically MgF_2 is favoured, the rate of MgO formation is faster than the rate of MgF_2 formation. This finding questions the validity of the computer predicted results for MTV combustion in the presence of air and highlights another limitation of the computer code - the total reliance on thermodynamics and the absence of kinetic factors. It should be noted that the incorporation of kinetic data in a computer code is complex and relies on detailed knowledge concerning each of many possible reaction processes. Thermodynamic modelling does however provide a useful indication concerning the direction of chemical reactions and in the absence of kinetic data allows the exploration of how the reactant composition and temperature influence the reaction products.

6.2 *Reaction Temperature*

The change in the reaction temperature with percentage magnesium displays a pronounced peak and the maximum temperature of approximately 3500 K occurs at the stoichiometric magnesium percentage (Fig. 12). This compares to approximately 3700 K at atmospheric pressure from calculations based on JANAF thermochemical tables, which also showed a maximum reaction temperature at a magnesium weight fraction of 0.33 [22].

Comparison of Figures 12 and 4 shows that the minimum mass of condensed phase reaction products is reached at the maximum reaction temperature where we expect the highest proportion of products in the gas phase. For the fuel rich formulations, as the reaction temperature decreases, the mass of condensed phase reaction products increases as expected. From Figures 1 and 2 the maximum reaction temperature corresponds to the maximum $MgF_2(g)$ product formed. Figure 13 also shows that the reaction temperature is not significantly altered by changes in the Viton content of the formulation from 1% to 10%.

The addition of oxygen (as air) to the reaction has a greater effect on the reaction temperature at lower pressures; increasing the air content to over 30% by mass generally increases the reaction temperature.

If the percentage Teflon is increased at the expense of the Viton (Fig. 15), the reaction temperature increases marginally due to the more positive heat of formation for Teflon compared to Viton.

6.3 *Heat of Reaction*

The maximum heat of reaction occurs at the stoichiometric magnesium percentage. Figure 16 shows the parabolic relationship between heat of reaction and the percentage fuel typical of a pyrotechnic formulation. At magnesium percentages greater than approximately 40%, the heat of reaction increases with increasing Viton content (Fig. 17). This effect is not due directly to the Viton. As the Viton percentage increases, the relative magnesium percentage decreases. From Figure 16, as the magnesium percentage decreases, the heat of reaction decreases. Below 40% magnesium, changes in the Viton

content have little effect on the heat of reaction.

The heat of reaction may be increased by including air as a reactant up to 20% air (Fig. 18). For the MTV formulation (54:30:16), addition of 20% air as a reactant significantly increases the heat of reaction from approximately 6.3 kJ/g to approximately 8.0 kJ/g. If MgO is formed in substantial amounts, as indicated by Eckstrom *et al.* [7], we would expect that the heat of reaction would not increase as much due to the more positive heat of formation of MgO compared to MgF_2. For percentages of air > 20%, the heat of reaction decreases significantly.

6.4 IR Decoy Flare Design

These results show that the maximum reaction temperature and the maximum heat of reaction occur near the stoichiometric MTV formulation, i.e. approximately 33% magnesium. Why then do standard extruded MTV decoy flares use a formulation based on 54% magnesium?

In the design of decoy flares, the amount of Viton in the formulation is largely governed by the manufacturing method. For example, if the flare is pressed, low percentages of Viton may be used; if the flare is extruded, larger quantities are required. This leaves the amount of magnesium and Teflon to be varied to meet the specification for the end use of the system. It would seem logical that the magnesium:Teflon ratio is based on three major requirements — ignitability, burn rate and performance (decoy effect).

Firstly, in the design of pyrotechnic systems it is usual to have a fuel rich system to enhance the system ignitability. Secondly, as Kubota *et al.* [22] have noted, the burn rate for MTV formulations increases with decreasing reaction temperature. Our results have shown that decreasing reaction temperature occurs for increased magnesium percentage. For decoy applications, the MTV formulation must have a very high burn rate which requires a high magnesium percentage. Also, pressure has little effect on the flare burn rate at high magnesium concentrations but can influence it at low magnesium mass fractions [22]. Finally, the IR output of MTV flares has been suggested to be largely due to the grey body radiation from the hot carbon particles [7]. Our results have shown that the mass fraction of C(s) is not very dependent on the percentage of magnesium for a wide range of temperatures and pressures. Therefore, high magnesium percentages do not significantly reduce the decoy effect of the MTV formulation.

These facts indicate that although the magnesium percentage in standard MTV compositions is far from ideal in terms of heat of combustion and reaction temperature, it has probably been optimized for burn rate and ignitability, while retaining acceptable decoy performance.

6.5 MTV Igniter Design

Although this report has concentrated on the use of MTV as an IR decoy flare composition, some comment on its use as a rocket motor (propellant) igniter composition is warranted. As noted previously, the preferred formulation for

MTV for this application is (61:34:5). Examination of Figures 1 to 18 again indicate that this approximate formulation does not appear to be optimized for reaction temperature, heat of reaction or mass of condensed phase reaction products. But, interestingly, the formulation appears to produce close to the maximum percentage MgF_2 (l) and some MgF_2 (s) both of which would be very efficient heat transfer media. The high magnesium content would impart good ignitability and a fast burn rate similar to the result for the IR decoy composition.

7. Conclusions

The theoretical study of the combustion of MTV compositions has shown that:

1. The major reaction products are MgF_2(s), Mg(s), and carbon.

2. Increasing the Viton content or replacing the Viton with Teflon has only minor effects on the reaction products.

3. The proportion of solid carbon produced is not very dependent on the formulation and temperature.

4. Changes in the combustion pressure mainly effect the equilibrium relationship between the gas and liquid phases of MgF_2 and Mg.

5. When burnt in air, it is difficult to predict the reaction product distribution principally due to the limited data base of the code, but also due to the need to include reaction kinetics in the composition.

6. The reaction temperature is at a maximum at the stoichiometric magnesium percentage, i.e. approximately 33%.

7. The reaction temperature increases marginally with increasing Viton or Teflon mass percentage when the proportion of magnesium remains constant.

8. The reaction temperature is greater in air than in an inert environment and it increases with increase in air concentration above 30% of total mass, particularly at low pressures. This conclusion may be affected by addition of Mg_3N_2 in the data base of the code and inclusion of reaction kinetics parameters.

9. The heat of reaction is a maximum at the stoichiometric magnesium percentage.

10. The heat of reaction is less when MTV is burnt in air (O_2 with inert N_2) than in an inert environment (argon).

11. The choice of 54% magnesium for the standard MTV decoy flare is probably to achieve high ignitability and burn rate rather than maximum reaction temperature or heat of reaction.

12. The choice of 61% magnesium for the standard MTV igniter composition is probably to achieve high MgF_2 (l + s) mass fraction for efficient heat transfer to the propellant surface rather than maximum heat of reaction or reaction temperature.

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A theoretical study of the combustion of magnesium/Teflon/Viton pyrotechnic compositions

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ABSTRACT

A theoretical study has been conducted using the NASA-Lewis CEC 76 computer code to model the combustion of pyrotechnic compositions based on magnesium/Teflon/Viton. The study examines the effect of formulation changes on the distribution of reaction products, the reaction temperature and the heat of reaction. The maximum temperature and heat are produced in the stoichiometric fuel concentration whilst the reaction products change significantly with the concentration of magnesium. The Teflon and Viton oxidizers generally have only a minor effect on the system thermodynamics.

The major reaction products are magnesium fluoride, magnesium and solid carbon. The proportion of carbon as a combustion product remains relatively constant over a large range of fuel or oxidant concentration.

The choice of the optimal MTV composition for IR decoy applications appears to be based more on burn rate and ignitability requirements than on temperature, heat output or optimization of reaction products.